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Hygroscopic growth and activation of HULIS particles: experimental data and a new iterative parameterization scheme for complex aerosol particles

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Abstract

The hygroscopic growth and activation of two HULIS and one Aerosol-Water-Extract sample, prepared from urban-type aerosol, were investigated. All samples were extracted from filters, redissolved in water and atomized for the investigations presented here. The hygroscopic growth measurements were done using LACIS (Leipzig Aerosol Cloud Interaction Simulator) together with a HH-TDMA (High Humidity Tandem Differential Mobility Analyzer). Hygroscopic growth was determined for relative humidities up to 99.75%. The critical diameters for activation were measured using LACIS for supersaturations between 2 and 10 per mill. All three samples showed a similar hygroscopic growth behaviour, and the two HULIS samples also were similar in their activation behavior, while the Aerosol-Water-Extract turned out to be more CCN active than the HULIS samples. The experimental data was used to derive parameterizations for the hygroscopic growth and activation of HULIS particles. The concept of ρ_{ion} (Wex et al., 2007a) and the Szyszkowski-equation (Szyszkowski, 1908; Facchini et al., 1999) were used for parameterizing the Raoult and the Kelvin (surface tension) terms of the Köhler equation, respectively. This concept proved to be very successful for the HULIS samples in the saturation range from relative humidities larger than 98% up to activation. However it failed for the Aerosol-Water extract.

1 Introduction

One important topic in current atmospheric research is to quantify the indirect aerosol effect and here especially how aerosol particles (natural and/or anthropogenic) may influence important cloud properties like cloud albedo (Twomey, 1974) or lifetime (Albrecht, 1989). For quantification of the indirect effect, the hygroscopic growth and activation behavior of atmospheric aerosol particles has to be known. In former studies this was investigated for inorganic substances like sodium chloride (NaCl) or ammonium sulfate ($(NH_4)_2SO_4$) (Rader and McMurry, 1986; Tang and Munkelwitz, 1994;

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Tang, 1996; Lance et al., 2006). Also organic substances, e.g. dicarboxylic acids and sugars, and simply mixtures were used in earlier investigations (Bilde and Svenningsson, 2004; Broekhuizen et al., 2004; Henning et al., 2005; Wex et al., 2007b). In the last years also humic-like substances (HULIS) came in the focus of cloud research. HULIS are composed of polymeric organic molecules with a large number of functional groups. The exact chemical composition of HULIS, which may also depend on the actual source process, is unknown. The concentration of HULIS in urban background varies between 0.3 and 1.6 μg/cm^3 (Samburova et al., 2005). Consequently, HULIS might contribute up to 60% of the organic mass of fine atmospheric aerosol particles (Kiss et al., 2005) and up to 54% of the water-soluble organic carbon (WSOC) (Salma et al., 2006). In investigations regarding the hygroscopic growth of HULIS particles, growth factors between 1.08 and 1.47 (depending on the source) were reported at a relative humidity of 90% (Dinar et al., 2007; Gysel et al., 2004). Also the activation of HULIS particles to cloud droplets has been the topic of recent research activities (Dinar et al., 2006b; Wex et al., 2007a; Asa-Awuku et al., 2007).

One problem dealing with HULIS is the existing spread regarding its material properties. The density of HULIS is reported to be between 1.4 g/cm^3 and 1.72 g/cm^3 (Asa-Awuku et al., 2007; Dinar et al., 2006a; Gysel et al., 2004). Published values for the molecular weight vary between 410 g/mol and 780 g/mol (Dinar et al., 2006b; Asa-Awuku et al., 2007; Samburova et al., 2005). Furthermore, HULIS lowers the surface tension of the solution (droplets). (Kiss et al., 2005; Salma et al., 2006; and Dinar et al., 2006b) reported reductions in surface tension by 25% to 42%.

Despite the past efforts, no consistent picture exists regarding the connection between hygroscopic growth and activation of HULIS particles. The surface tension that were needed to achieve a consistent description from hygroscopically grown to activated particles differed in the different studies (Dinar et al., 2006b; Wex et al., 2007a; Asa-Awuku et al., 2007). Therefore, in this work, we extent the hygroscopic measurements to the relative humidity range larger than 98%, i.e., to the range that has to be considered when examining the possible influences of surface tension on hygroscopic

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particle growth.

In the following, we describe the investigation of the hygroscopic growth and activation of two HULIS and one Aerosol-Water-Extract sample, all of them taken downtown Budapest, Hungary. The first HULIS sample was sampled in spring 2005, while the second sample for HULIS and the Aerosol-Water-Extract were taken in summer 2006. All samples were extracted from filters, redissolved in water and atomized for the investigations presented here. The hygroscopic growth measurements were done using LACIS (Leipzig Aerosol Cloud Interaction Simulator) together with a HH-TDMA (High Humidity Tandem Differential Mobility Analyzer). Hygroscopic growth was determined for relative humidities up to 99.75%. The critical diameters for activation were measured using LACIS for supersaturations of approximately 2, 4, 6, 8 and 10 per mill. Based on the experimental data, a parameterization that consistently describes the hygroscopic growth and the activation of HULIS particles will be presented.

2 Experimental setup and procedure

For the investigation regarding the hygroscopic growth and activation of HULIS and Aerosol-Water-Extract particles presented here, two different instruments, a) a High-Humidity Tandem DMA (HH-TDMA) (Hennig et al., 2005) and b) the Leipzig Aerosol Cloud Interaction Simulator (LACIS) (Stratmann et al., 2004) were used. The HH-TDMA was applied to measure the hygroscopic growth below 98% relative humidity while LACIS was utilized to investigate the hygroscopic growth between 98% and 99.75% relative humidity and to determine the critical diameter for activation at several supersaturations from 2 to 10 .

The version of LACIS used for this study consists of a flow tube of 1 m length. Aerosol and sheath air were humidified (aerosol: MH-110-12S-4, sheath air: PH-30T-24KS, Perma Pure) to well defined dew point temperatures (reproducibility approx. 0.01 K) before entering the flow tube. The dew point temperatures and the LACIS wall temperature determine the water-vapor-saturation or the maximum supersaturation in the flow

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tube. For the hygroscopic growth measurements described here, LACIS was operated in its sub-saturated mode of operation (Wex et al., 2005). In this mode the wall temperature (20°C) is above the dew point temperature (between 19.67°C and 19.97°C) of the aerosol and the sheath air. While passing through the flow tube, particles reach their equilibrium diameter for the adjusted relative humidity (RH). The supersaturated mode of operation was applied for the activation measurements (Wex et al., 2006). In contrast to the sub-saturated mode, the wall temperature (here varied between 5.51°C and 5.82°C) is below the dewpoint temperature (22.0°C) of the aerosol and the sheath air. With increasing water vapor saturation (decreasing wall temperature) the maximum saturation reached in LACIS increases. The particles activate in LACIS, if the maximum saturation reached is equal or above their critical supersaturation. At the LACIS outlet, an optical particle spectrometer measures the size of the grown particles (Kiselev et al., 2005). For the investigations presented here, the spectrometer was calibrated before and after the campaign using PSL particles of 7 different sizes between 203 nm and 2390 nm (Duke Scientific) and SiO_2 particles with diameters between 490 nm and 1570 nm (Duke Scientific), respectively. Results of both calibrations were virtually identical. The refractive index used to retrieve the droplet size from the measured scattered light intensities was 1.65 for HULIS (Hoffer et al., 2006) and 1.53 for the Aerosol-Water-Extract. When determining the sizes of the hydrated particles, a change of the refractive index with increasing size was taken into account by using a volume mixing rule, as described in Kiselev et al. (2005). Therefore, using 1.65 as refractive index for the Aerosol-Water-Extract lowered the measured hygroscopic growth by less then 10 nm (less than 3%) and had no influence on the determined supersaturations, due to the solution of the hydrated particles/droplets that get more diluted as the particles grow. To calibrate the relative humidity and the supersaturation in LACIS for the different temperature set-ups used during the measurements, ammonium sulfate particles were used prior to the experiments.

A special version of an Humidity Tandem Differential Mobility Analzyer (HTDMA) was used in this study, the high humidity TDMA (HH-TDMA), which is described in detail

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in Hennig et al. (2005). The specific feature of this HH-TDMA consisted of a temperature controlled humidification system that was operated at 18°C. The Differential Mobility Analyzers (DMA) measuring the hydrated particle sizes operated in a temperature controlled water bath at 18°C. The humidification system was regulated separately for for the aerosol and for the sheath air of the second DMA. The sheath air was a mixture of dry synthetic air and high RH synthetic air previously lead through a water-to-gas humidifier (PH series, ANSYCO). The aerosol was humidified in a gas-to-gas humidifier (PD series, ANSYCO). The RH for both the aerosol and the sheath air for the second DMA where controlled by regulating the mixing ratio of the dry and the wet air. Due to the slightly higer temperature in the humidification section compared to that in the water bath around the DMA, high RH values could be used for measurements, which otherwise would be difficult, due to the limitation of water permeability through the humidifier membranes. HH-TDMA measurements of the HULIS samples and of the Aerosol-Water-Extract were performed at relative humidities between 80% and 98%. Before and after the measurements, calibration scans were made using ammonium sulfate.

To collect the particle material investigated in this study, two aerosol samples ($PM_{2.5}$) were taken in downtown Budapest, Hungary, applying a high-volume sampler with Whatman QM-A quartz fiber filters. The filters were heated prior to sampling, to remove possible contaminants. The first sample was taken during spring 2005 in the non-heating season and only HULIS was extracted by means of a modified solid-phase extraction protocol Varga et al. (2001). Concerning the second sample, which was taken in summer 2006, again HULIS was extracted from a part of the filter. For further details on the extraction scheme for the HULIS samples, the reader is referred to Salma et al. (2006) and Salma et al. (2007). Additionally, for the sample taken in summer 2006, all water soluble material (named Aerosol-Water-Extract in the framework of this paper) was extracted from another quarter section of the same filter. For this, the quartz filter sample was extracted by high-purity reagent water (Milli-Q) for about 48 h in two steps. The joint water extract was filtered through a PVDF syringe membrane

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filter with a pore size of 0.22 μm to remove the filter debris and suspended insoluble particles. The solution was freeze-dried immediately after the filtration at a temperature of liquid nitrogen and it was kept frozen during storage and transport.

To generate the HULIS and Aerosol-Water-Extract particles investigated, the extracted samples were dissolved in double de-ionized Milli-Q water with an additional reduction of total organic carbon (TOC) (18.2 MOhm, TOC<4 ppb). The solution was atomized by means of an atomizer (type TSI 3075). The generated solution droplets were dried (below 13% relative humidity) utilizing a diffusion dryer and size selected by means of a DMA (Differential Mobility Analyzer, type Vienna Medium). Finally, the size selected particles were supplied to the HH-TDMA and LACIS. For the hygroscopic growth measurements, dry particle diameters of 200 nm for the first and 230 nm for the second HULIS sample were selected for the LACIS measurements, while 165 nm was used for them LACIS measurements of the Aerosol-Water-Extract. For the HH-TDMA measurements, dry diameters of 100 nm for the first HULIS sample and 100 nm and 230 nm for the second HULIS sample were used, while 100 nm particles were selected for the Aerosol-Water-Extract. To study the activation behaviour of both HULIS and Aerosol-Water-Extract particles, the dry diameter of the particles was varied between 25 and 200 nm.

3 Measurement results

In this section the results of the measurements performed regarding the hygroscopic growth and activation behavior of the investigated HULIS and the Aerosol-Water-Extract samples are presented and discussed.

3.1 Hygrocopic growth

Figure 1 depicts the results of the hygroscopic growth measurements. Given are the measured growth factors (corresponding to the ratio of wet to dry particle diameters,

$d_p/dp_{p,0}$) as function of relative humidity. Here the results of LACIS (diamonds) and H-HTDMA measurements (triangles) are shown. As to be seen, the growth factors of both HULIS samples are comparable, although the hygroscopic growth of the first sample exceeds that of the second sample slightly (Fig. 1, upper panel). Particles from the second HULIS sample with dry sizes of 100 nm show a slightly larger growth factor than the according particles with dry sizes of 230 nm, due to the Kelvin effect, but the difference in the growth factors between these dry particle sizes was within measurement uncertainty. Particles generated from the Aerosol-Water-Extract exhibit slightly larger growth factors compared to the corresponding HULIS particles from the second sample (Fig. 1, lower panel). For relative humidities above 97%, the growth factor of the Aerosol-Water-Extract particles starts to slightly exceed even that of the first HULIS sample. This enhanced hygroscopic growth of the Aerosol-Water-Extract particles can be explained by the fact, that they consist of a mixture of HULIS, low molecular weight organics and inorganic substances. The inorganic substances and low molecular weight organics may enhance the hygroscopic growth of the Aerosol-Water-Extract particles compared to the HULIS particles.

The hygroscopic growth of HULIS particles at lower relative humidities was investigated before. Reported growth factors lie between 1.08 and 1.47 at a relative humidity of 90% (Dinar et al., 2007; Gysel et al., 2004). Depending on the sample source the growth factors vary. For example, fresh HULIS from wood fires (i.e. biomass burning, where the HULIS is supposed to originate as a primary aerosol) has a growth factor of 1.18, while the growth factor of HULIS extracted from aged wood burning particles is 1.24 and from background particles 1.47 (Dinar et al., 2007). Our growth factors at a relative humidity of 90% for the first and second HULIS sample are 1.17 and 1.05, respectively, which agrees with the formerly reported values. Measured growth factors for Aerosol-Water-Extract at a relative humidity of 90% vary between 1.48 and 1.52 (Gysel et al., 2004). At a relative humidity of about 90%, our growth factor is systematically smaller, i.e., 1.11 for the Aerosol-Water-Extract. This underlines the fact, that the properties of both HULIS and Aerosol-Water-Extract may vary as function of sample lo-

cation. In urban air, where our samples originated from, HULIS is thought to be formed mainly as secondary aerosol by chemical reactions followed by oligomerization and polymerization. Indeed, the water-soluble organic carbon (WSOC) for the sampling location in summer 2006 accounted for (32+/–8)% of the organic carbon (OC), which is substantially less than for aerosol that originating from main sources other than road traffic (Salma et al., 2007). The mean WSOC/OC concentration ratios for continental background sites, and for tropical biomass burning aerosols were up to about 70%. Such variations in the abundance of oxygenated (and thus more water soluble) organics in samples of dissimilar origin can definitely cause differences in the hygroscopic properties of HULIS and of Aerosol-Water-Extract as well.

3.2 Activation

The critical saturations of water vapor needed for the activation of HULIS and Aerosol-Water-Extract particles are shown in Fig. 2. Plotted are critical saturations as function of dry particle size. Vertical error bars correspond to the standard deviation as derived from the results of three independent measurements. Horizontal error bars correspond to half the step-size applied when scanning dry diameters during the activation measurements. Analogous to the results of the hygroscopic growth measurements, the activation behavior of both HULIS samples is similar. At the same water vapor saturation the dry diameter of the particles that activate is significantly smaller for the Aerosol-Water-Extract particles in comparison to the HULIS particles. At a water vapor saturation of about 1.004, the critical diameter for activation was found to be 37.5 nm for the Aerosol-Water-Extract and 92.5 nm for the HULIS particles. I.e., consistent with the observed hygroscopic growth, particles generated from Aerosol-Water-Extract are clearly more CCN-active. Again, the explanation for this behavior is most likely the presence of low molecular weight organics and inorganics in the Aerosol-Water-Extract particles which enhances the CCN-activity (Asa-Awuku et al., 2007).

We also compared our results to those of two other studies examining particles consisting of HULIS extracted from atmospheric aerosol samples. In these studies, HULIS

extracted from particles sampled in Israel (Dinar et al., 2006b) and the USA (Asa-Awuku et al., 2007) were considered. In both studies the HULIS particles were found to be more CCN active than in our investigation. At a supersaturation of roughly 1% we observed activation for particles with dry diameters of 50 nm (first HULIS sample) and 46 nm (second HULIS sample). For the same supersaturation, in the earlier studies, particles with dry diameters between 33 nm and 40.6 nm were activated. At a supersaturation of about 0.5% our first HULIS sample activated at 75 nm dry diameter while critical diameters reported in the earlier studies are 47.5 nm and 69.6 nm. At 0.2 % supersaturation we found a critical diameter of 165 nm and the values reported earlier vary between 81 nm and 133 nm. These differences are most likely due to the different source processes and the resulting different compositions of the HULIS samples (Graber and Rudich, 2006).

In conclusion, although the HULIS samples investigated in this study show comparable hygroscopic growth and activation behaviour, this is not necessarily the case for HULIS in general, since HULIS particles from different origins may vary significantly.

4 Theory

4.1 Background

The hygroscopic growth of particles can be described by the Köhler theory (Köhler, 1936). The Köhler Eq. (1) combines an increase of the water vapor pressure above a curved surface with a decrease of the water vapor pressure over an aqueous solution surface. These effects are called Kelvin and Raoult effect, respectively.

$$S = \exp\left(\frac{4M_w\sigma}{RT\rho_w d_p} - \frac{v\phi n_s}{n_w}\right) \quad (1)$$

Here, S is the water vapor saturation over the droplet surface, M_w the molecular weight of water, R the universal gas constant, T the absolute temperature, d_p the particle

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diameter and ρ_w the density of pure water. Furthermore, σ is the surface tension of the solution, ν the number of ions a molecule dissociates in solution, ϕ the osmotic coefficient and n_s and n_w the number of moles from the solute and water, respectively. The number of moles of solute can be rewritten as

$$n_s = \frac{\pi \rho_s d_{p,0}^3}{6 M_s} \tag{2}$$

with the density and the molecular weight of the solute ρ_s and M_s, and with the dry particle diameter $d_{p,0}$. Thus, with Eq. (2) the Köhler Eq. (1) becomes

$$S = \exp\left(\frac{4 M_w \sigma}{RT \rho_w d_p} - \frac{\nu \phi \rho_s M_w}{\rho_w M_s} \frac{d_{p,0}^3}{d_p^3 - d_{p,0}^3}\right) \tag{3}$$

Here $d_{p,0}$ and d_p are the diameters of the dry and the wet particle, respectively.

The unknown quantities in Eq. (3) are the surface tension of the solution (σ), the number of ions a molecule dissociate and the osmotic coefficient (ν and ϕ). Also, the molecular weight and the density of the solute (M_s and ρ_s) are often unknown when atmospheric particles are considered. The unknown quantities in the second term of the Köhler Eq. (3) can be summarized in a single parameter ρ_{ion}, which was established by Wex et al. (2007a) and is defined as

$$\rho_{\text{ion}} = \frac{\nu \phi \rho_s}{M_s} \tag{4}$$

The surface tension can be parameterized by the Szyszkowski-Langmuir equation (Szyszkowski, 1908; Facchini et al., 1999)

$$\sigma = \sigma_{\text{water}} - aT \ln(1 + bC) \tag{5}$$

were σ_{water} is the surface tension of pure water, a and b are the Szyszkowski-parameters and C the concentration of the solution in moles of solute per mass of

water. The concentration of the solution can be substituted by

$$C = \frac{\rho_s}{M_s \rho_w} \frac{d_{p,0}^3}{d_p^3 - d_{p,0}^3} \tag{6}$$

With Eq. (6), the Szyszkowski Eq. (5) can be rewritten as

$$\sigma = \sigma_{\text{water}} - aT \ln \left(1 + b' \frac{d_{p,0}^3}{d_p^3 - d_{p,0}^3} \right) \tag{7}$$

The new parameter b' combines the "old" Szyszkowski parameter b with the unknown properties of the solute and the density of water:

$$b' = b \cdot \frac{\rho_s}{M_s \rho_w} \tag{8}$$

For substances like HULIS with unknown dissociation behavior, density and molecular weight, which influence the surface tension of the solution, a rearranged form of the Köhler equation can be written when applying Eqs. (7) and (4). This equation will be used in the parameterization procedure described below.

$$S = \exp \left(\frac{4 M_w \left(\sigma_{\text{water}} - aT \ln \left(1 + b' \frac{d_{p,0}^3}{d_p^3 - d_{p,0}^- 3} \right) \right)}{RT \rho_w d_p} - \frac{\rho_{\text{ion}} M_w}{\rho_w} \frac{d_{p,0}^3}{d_p^3 - d_{p,0}^3} \right) \tag{9}$$

It should be noted, that possible partitioning effects (Sorjamaa et al., 2004) on both the Raoult and the Kelvin term are not treated explicitly here. However, if these effects are important they will influence the parameters ρ_{ion}, a and b' implicitly.

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4.2 An iterative scheme to retrieve a parameterization

The hygroscopic growth of aerosol particles is more influenced by the Raoult effect, i.e., the number of molecules in the solution, than by the Kelvin effect, i.e., the effect of the surface tension. In contrast, considering the activation of aerosol particles, the influence of the Kelvin term maybe larger than that of the Raoult term. Taking advantage of this, we developed an iterative scheme to derive ρ_{ion} and the parameters a and b' of the Szyszkowski Eq. (7) from the combination of both, hygroscopic growth and activation measurements. The iterative scheme can be outlined as follows:

- determination of a first guess for ρ_{ion} using a re-arranged form of Eq. (9), i.e.,

$$\rho_{\text{ion}} = \frac{\rho_w \left(d_p^3 - d_{p,0}^3\right)}{M_w d_{p,0}^3} \cdot \frac{4M_w \left(\sigma_{\text{water}} - aT \ln\left(1 + b' \frac{d_{p,0}^3}{d_p^3 - d_{p,0}^3}\right)\right)}{RT\rho_w d_p} - \ln(S) \quad (10)$$

  assuming the surface tension σ to be that of pure water, i.e., 72.8 mN/m (a=0) and considering only the equilibrium diameters measured with LACIS at the highest relative humidities (RH between 98.25% and 99.7%).

- adjustment of the Szyszkowski-parameters a and b' by minimizing the least square difference between the measured and the calculated (Eq. 9) critical supersaturations needed for activation.

- calculation of ρ_{ion} using the Szyszkowski-parameters a and b' as determined in the previous step.

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– repetition of steps two and three until convergence is reached for ρ_{ion} and the Szyszkowski-parameters a and b'.

The procedure yields a parameterization for hygroscopic growth and activation of aerosol particles, based on ρ_{ion} and the Szyszkowski-parameters a and b' being fitted to consistently describe experimental hygroscopic growth and activation data. However, the procedure relies on the assumption of a constant ρ_{ion} in the high (larger than 98%) relative humidity range. The validity of this assumption will be discussed below.

5 Results of parameterization

Utilizing the experimental data and the parameterization approach described above, values for ρ_{ion} and the Szyszkowski-parameters a and b' were determined for the two HULIS samples and the Aerosol-Water-Extract.

5.1 HULIS

Figures 3 and 4 depict the results obtained regarding the parameterization of the activation behavior for the two HULIS samples investigated. Plotted are critical saturations as function of dry particle diameter. Given are the measured values (symbols) and the results of the parameterization (lines).

Theoretical curves for three different values of ρ_{ion} (and as a consequence, three different values for the Szyszkowski parameters a and b') are shown. These three parameter sets were determined using, in the iteration scheme, the three different growth factors (highest, middle, lowest humidity) determined experimentally with LACIS in the RH range larger than 98%. As to be seen, each of the three parameter sets produced comparable results for the activation behavior. This is a strong indication that the assumption of a constant ρ_{ion} in the high RH regime might be justified for the HULIS samples investigated here. In general, the agreement between the measured and the

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calculated values is very good for both samples underlining the applicability and validity of the parameterization scheme suggested here.

Figures 5 and 6 depict the corresponding results regarding the hygroscopic growth behavior of the two HULIS samples. Plotted are measured and calculated growth factors as function of relative humidity. Here again growth factors measured with the HH-TDMA (triangles) are included and calculated curves (lines) for the three different parameter sets are given.

Again, the agreement between the measured and the calculated growth factors is strikingly good supporting the assumption of a constant ρ_{ion} in the high RH regime. However, for RHs below 98% significant differences between the measured and calculated growth factors start to occur, especially for the second HULIS sample. These differences could be explained as being a result of using two different instruments, i.e., LACIS and the HH-TDMA. However, as will be discussed below, there is evidence that this is not the case and therefore the occurring deviations might be attributed to an increasingly non-ideal behaviour of the solution droplets resulting in e.g. a variable osmotic coefficient and consequently a variable ρ_{ion}. Another effect which could cause the observed differences would be the presence of slightly soluble compounds in the HULIS samples.

Tables 1 and 2 summarize the parameters determined during the parameterization effort and the derived surface tensions at the point of activation, respectively.

From the given values it can be concluded that, the differences between the two HULIS samples seem to mainly arise from differences in the surface tension and that the surface tensions at the point of activation can be significantly lower than that of water especially for smaller dry particle diameters and consequently smaller and higher concentrated droplets. This is in agreement with the results given in Wex et al. (2007a).

5.2 Aerosol-Water-Extract

The parameterization approach successfully used to parameterize the two HULIS samples as outlined above was also applied to the data gained regarding the activation and

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the hygroscopic growth of particles generated from the Aerosol-Water-Extract. Figures 7 and 8 depict the results, i.e., the measured and calculated critical saturation as function of particle dry diameter and particle growth factors as function of relative humidity, respectively.

As to be seen from Fig. 7, although the iterative procedure converged, the determined values for ρ_{ion} and the Szyszkowski parameters a and b' are not suitable to describe the activation behavior of the Aerosol-Water-Extract. This is in line with the findings of Asa-Awuku et al. (2007) and implies that HULIS, although being present in the sample, may not be the species controlling the hygroscopic growth and activation behavior of the Aerosol-Water-Extract.

Despite the fact that the activation behavior is described rather poorly, the hygroscopic growth (Fig. 8) is predicted with good accuracy. This holds even down to relative humidities around 97% and consequently into the RH range investigated utilizing the HH-TDMA. This a) makes experimental artefacts due to the usage of two different instruments, i.e., LACIS and the HH-TDMA, unlikely and b) again suggests a variable ρ_{ion} in the lower RH range.

Speculating, with respect to possible explanations for the observed behavior of the Aerosol-Water-Extract, two reasons seem possible: a) the assumption of a constant ρ_{ion} may not be adequate for the Aerosol-Water-Extract investigated here, i.e., even at RHs larger than 99% non-ideal behavior may occur and/or there might still be a undissolved or slowly dissolving core inside the droplets; b) the Szyszkowski equation might not have the correct functional form to describe the surface tension-concentration relation valid for the droplets near activation. This could be attributed to a salting-out effect as also described by Asa-Awuku et al. (2007). Salting-out might cause an enrichment of the surface active components of the Aerosol-Water-Extract (namely the HULIS fraction) at the droplet surface and might lower the surface tension excessively, to an extent that can not be captured with the Szyszkowski approach any more. Of course, also a combination of the two effects a) and b) is possible. However, this will be the topic of future investigations and could not be investigated in more detail within

the scope of this paper simply because of the limited availability of the Aerosol-Water-Extract.

6 Summary and conclusions

In this study the hygroscopic growth and activation behavior of particles generated from two HULIS and one Aerosol-Water-Extract sample were investigated utilizing both, LACIS and a HH-TDMA. The samples were taken in downtown Budapest, Hungary. The first HULIS sample was collected in spring 2005. The second HULIS sample and the Aerosol-Water-Extract were extracted from the same filter, which was collected in summer 2006.

The hygroscopic growth and activation behavior of both HULIS samples was found to be comparable, although they were taken at different times. Particles generated from Aerosol-Water-Extract show a slightly larger hygroscopic growth than the associated HULIS particles and are more CCN active compared to particles from both HULIS samples. Inorganic compounds and low molecular weight organics can be a reason for this behavior of the Aerosol-Water-Extract. Comparing our results to those available in the literature we found, that our HULIS and Aerosol-Water-Extract samples featured systematically smaller growth factors and were less CNN active. This underlines the fact, that the properties of both HULIS and Aerosol-Water-Extract samples may vary as function of sample location and formation process.

Based on the Köhler equation and the measured hygroscopic growth and activation behavior, an iterative scheme was developed for deriving a consistent parameterization to describe the hygroscopic growth and activation of complex aerosol particles with unknown or partly unknown material properties. The iterative procedure relies on the concepts of ρ_{ion} and the Szyszkowski equation, to parameterize the Raoult- and the Kelvin-terms in the Köhler equation. When HULIS particles were considered, the procedure and the resulting parameterizations were found to work nicely with respect to the description of activation and hygroscopic growth in the high RH regime. However,

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for RHs below 98%, gained results indicate a non-ideal behavior of the solution droplets resulting in a variable, i.e., concentration and particle size dependent ρ_{ion}. Considering the Aerosol-Water-Extract sample, the parameterization scheme failed to predict the activation behavior. This is suggestive for a) non-ideal behavior of the Aerosol-Water-Extract particles even at RHs larger than 99% and/or b) the the Szyszkowski equation not being the proper function to describe the surface tension near activation, possibly due to salting-out effects.

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Table 1. Szyszkowski-parameters and ρ_{ion} for the two HULIS samples.

Substance	a [1/K]	b	ρ_{ion}[mol/m^3]
HULIS, first sample	9.505×10^{-6}	100	5434
HULIS, second sample	2.14×10^{-5}	100	5268

Table 2. Calculated surface tension at the point of activation for the two HULIS samples.

Substance	dry diameter [nm]	surface tension [mN/m]
HULIS, first sample	50	67.8
HULIS, first sample	75	69.1
HULIS, first sample	100	69.6
HULIS, first sample	125	70.3
HULIS, second sample	46	60.9
HULIS, second sample	47.5	62.0
HULIS, second sample	62.5	63.3
HULIS, second sample	92.5	65.2
HULIS, second sample	165	67.9

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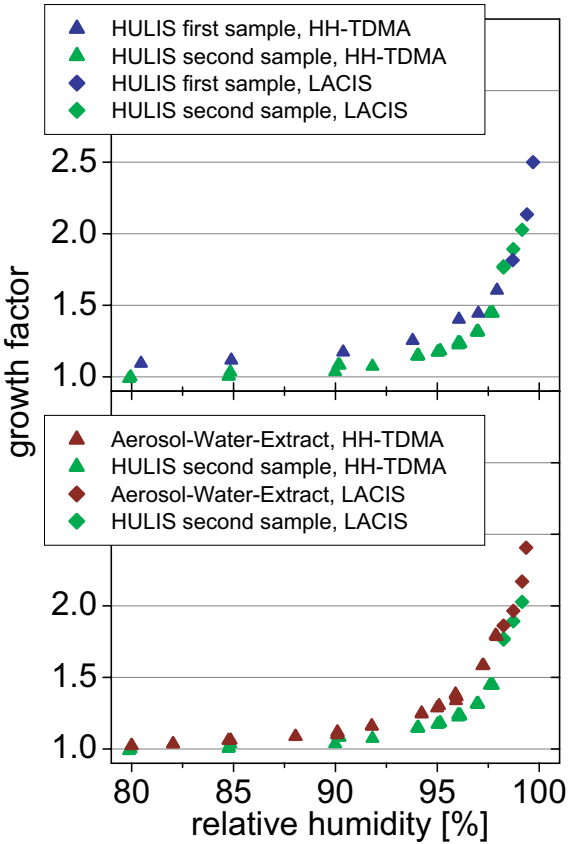

Fig. 1. Hygroscopic growth factors measured with LACIS (diamonds) and the HH-TDMA (triangles) as function of relative humidity for particles from the two HULIS and the Aerosol-Water-Extract samples. The different dry sizes used in the different measurements are given in the text.

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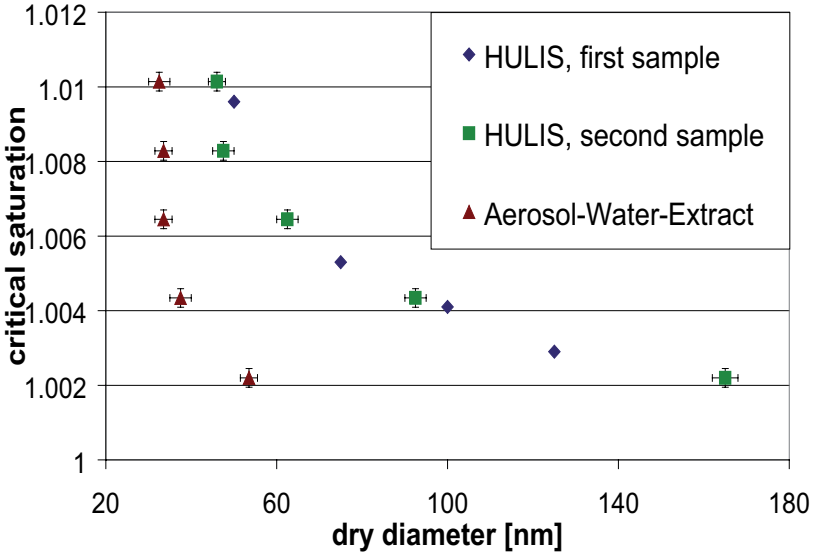

Fig. 2. Critical saturations needed for the activation measured with LACIS as function of dry diameters for both HULIS-samples and the Aerosol-Water-Extract.

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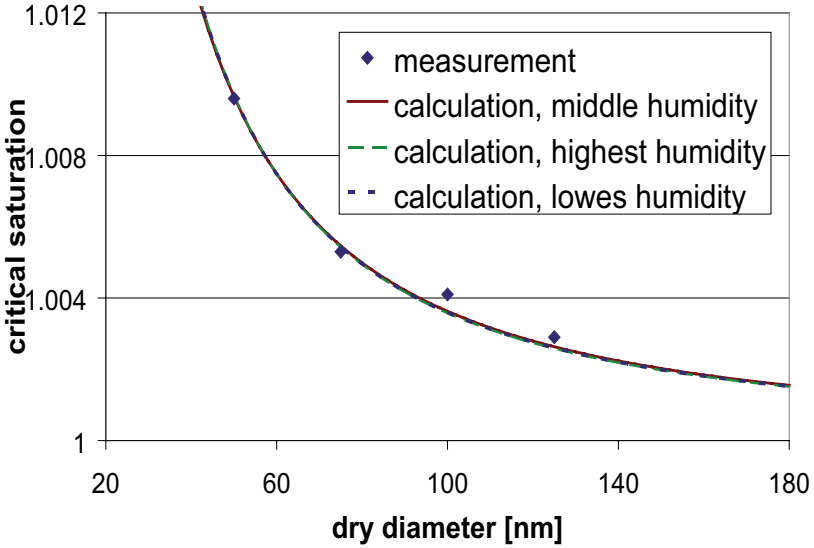

Fig. 3. Measured (symbols) and calculated (lines) critical saturations as function of dry particle diameter for the first HULIS sample.

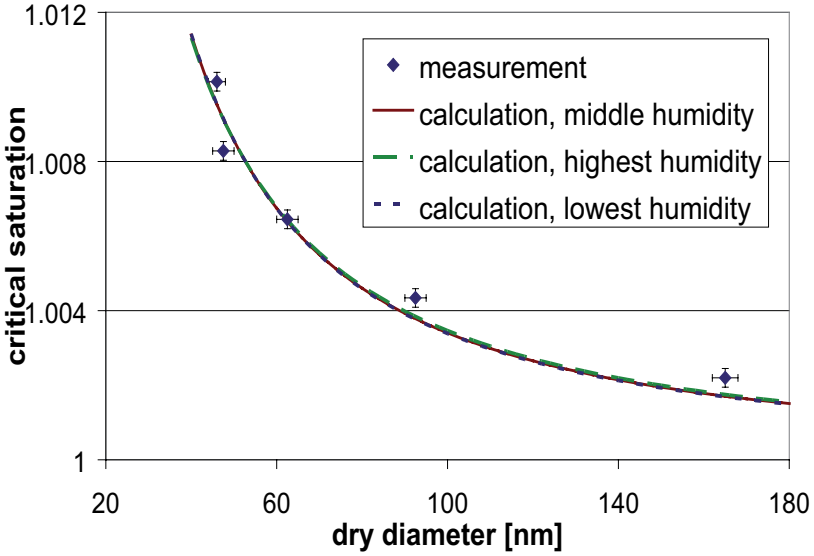

Fig. 4. Measured (symbols) and calculated (lines) critical saturations as function of dry particle diameter for the second HULIS sample.

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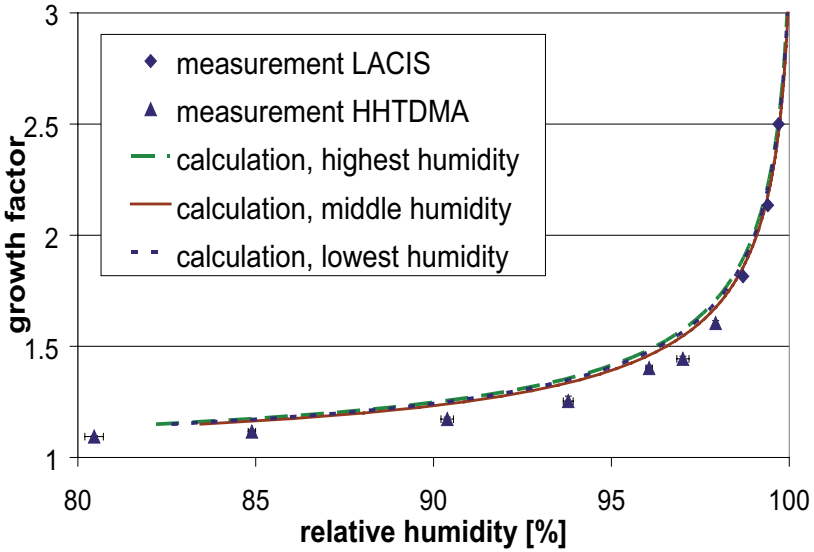

Fig. 5. Measured (symbols) and calculated (lines) growth factors as function of relative humidity for the first HULIS sample (dry diameters: LACIS 230 nm, HH-TDMA 100 and 230 nm).

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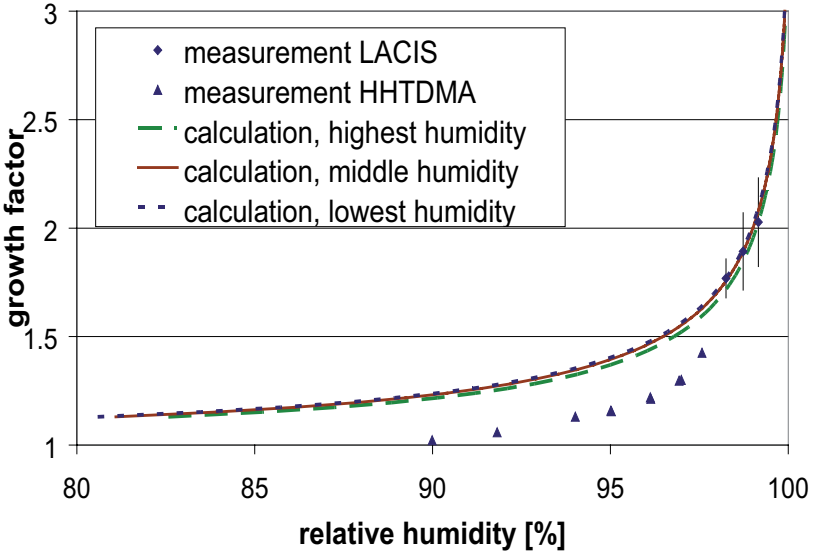

Fig. 6. Measured (symbols) and calculated (lines) growth factors as function of relative humidity for the second HULIS sample (dry diameters: LACIS 230 nm, HH-TDMA 100 and 230 nm).

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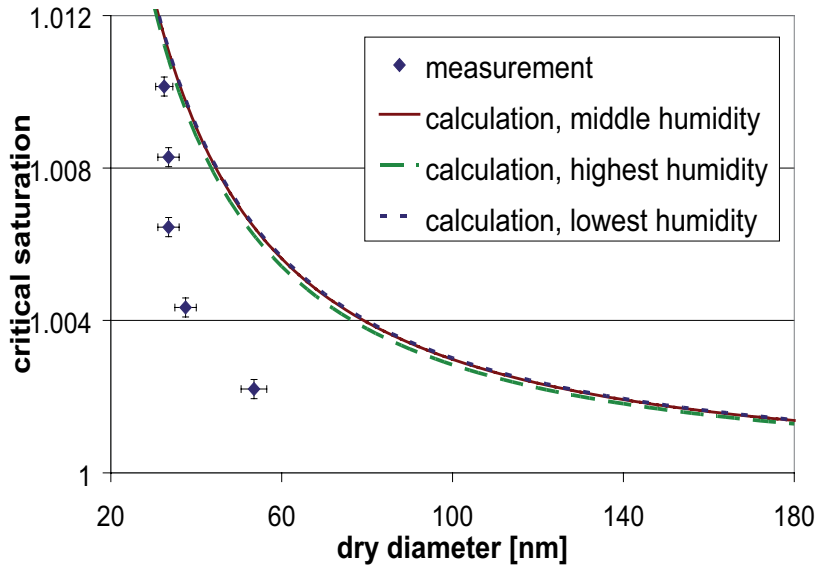

Fig. 7. Measured (symbols) and calculated (lines) critical saturations as function of dry particle diameter for the Aerosol-Water-Extract sample.

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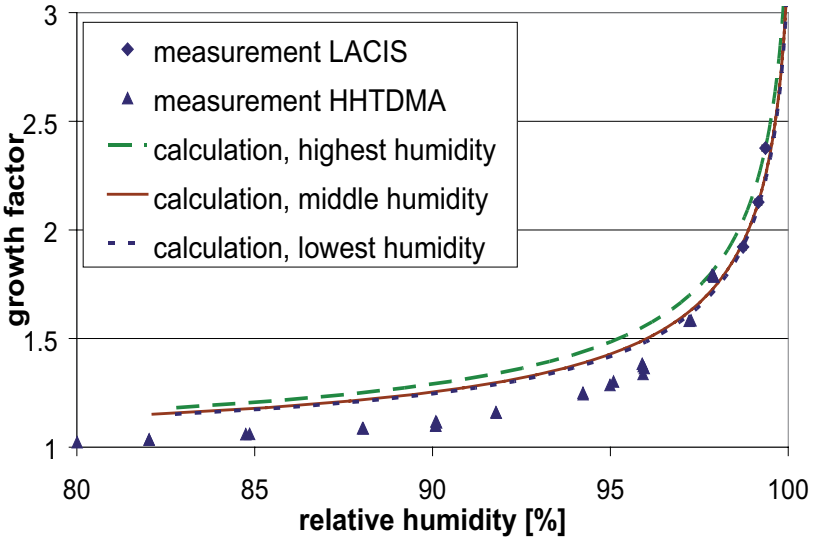

Fig. 8. Measured (symbols) and calculated (lines) growth factors as function of relative humidity for the Aerosol-Water-Extract sample (dry diameters: LACIS 165 nm, HH-TDMA 100 nm).

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